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Comparison of effective conductivities calculated by the effective medium approximation and the self consistent approximation for core-shell particulate composites

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The effective conductivity of composites containing simple or core-shell particles has been estimated in the literature using the Mean Field Approximation (MFA) and the Self-Consistent Approximation (SCA) among other techniques. It is shown here that for both simple and core-shell particles the two approximations agree to first order in the particle volume fraction but differ at the second order term. For simple particles the coefficient of the second order term calculated by SCA is at much better agreement with previous exact results than the coefficient calculated by MFA. For core-shell particles the results of the two approximations are almost identical up to particle volume fraction 0.20 but diverge with increasing volume fraction and particle-to-matrix conductivity ratio. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/1.4999331>

I. INTRODUCTION

There is a vast literature on effective properties of particulate composites, especially for mechanical and electrical/optical properties which concern the majority of applications. Historical survey and extensive references on the dielectric properties of composites are included in Sihvola, Ref. 1. For mechanical properties of composites Giordano, Ref. 2 presents a theory for arbitrary microstructures characterized solely by the volume fraction and the properties of the component phases and the compares with previous work. The present paper is limited to the simpler problem of electrical conductivity but the results equally apply to thermal conductivity and diffusivity when the constitutive equations are linear.

For spherical and uniformly sized dispersed particles Maxwell in Ref. 3 derived by an intuitive argument his often quoted equation for the effective electrical conductivity which is correct only to first order in the particle volume fraction. Much later Ref. 4 gave a straightforward derivation of the thermal conductivity exact to first order in the particle volume fraction. A similar equation for the electrical permittivity is known as the Maxwell-Garnett formula, Ref. 1. At this so called dilute limit particle-particle interactions are neglected implying independence from the spatial particle distribution. To obtain results to higher order in the volume fraction it is necessary to specify the spatial particle distribution. For random spatial distribution of particles (hard sphere distribution) Jeffrey, Ref. 5 derived an expression *exact to second order* in the volume fraction. There is an extensive literature on approximate methods dealing with non-dilute dispersions of spheres where the spatial particle distribution is also considered, e.g. Refs. 6 and 7.

At volume fractions above the dilute limit Hashin, Ref. 8 derived simple approximate results for the effective conductivity using SCA. This version of SCA involves an additional unspecified parameter for a certain value of which the results are in good agreement with the results of Jeffrey (1973) to second order in the particle volume fraction, see also Ref. 9. Other SCA approaches are discussed in Ref. 10. The self-consistent approach implicit in expressions for the effective mechanical properties of multi-grained materials, Ref. 2, differs from the more special SCA of Ref. 8 used in the present paper.

The case of simple spherical particles having interfacial thermal resistance has also been investigated. In the dilute limit the analysis involves only a slight modification of the basic equations, Ref. 11, while higher particle volume fractions were treated by a self-consistent scheme in Ref. 10.

Composites containing dispersed ellipsoidal particles are included in Ref. 12 which analyzed composites with coated ellipsoidal particles by MFA employing averaging over orientations. Composites of isotropic but otherwise general microstructural geometry have been treated by several authors. Hashin and Strickland, Ref. 13 derived upper and lower bounds for the effective magnetic permeability of such composites. The bounds obtained, which also apply to conductivity are independent of the detailed geometry. For the particulate spherical geometry the bounds are the tightest possible and, as suggested by a reviewer, expansions in the volume fraction of the dispersed phase coincide and are in agreement with the first order term in Maxwell's equation.

The effective permittivity of a composite of coated spheres (core-shell) was treated in the dilute limit in Ref. 14 by first deriving the permittivity of an equivalent simple sphere (internal homogenization") and using that permittivity to derive the effective permittivity of the composite ("external homogenization"). The effective conductivity of core-shell particles was investigated in Ref. 15 in a general setup that includes anisotropic particle cores. The MFA employed in this study utilizes an internal homogenization step that simplifies the derivation but is not essential to the MFA. Reference 16 treated the optical properties of two dimensional composites containing randomly dispersed core-shell cylinders. At the limit of large wave length and low cylinder volume fraction MFA yields results consistent with the classical Maxwell-Garnet formula.

MFA and SCA are simple and popular approximations for the effective conductivity but there has not been a direct comparison in terms underlying assumptions and accuracy. In the present paper we extend SCA to core-shell particles and compare the results with the corresponding MFA results. Section II reviews well known results for simple spherical particles and compares with the exact results of Ref. 5. Section III reviews the underlying assumptions of the MFA and SCA for core-shell particles, and section IV provides numerical comparisons.

II. THE MFA AND SCA FOR SIMPLE SPHERICAL PARTICLES TO SECOND ORDER IN THE VOLUME FRACTION

The only exact results to second order in the particle volume fraction v are those of Ref. 5:

$$\frac{\sigma^*}{\sigma_m} = 1 + 3\beta v + 3\beta^2 (1 + F(\alpha)) v^2 + O(v^3) \quad (1)$$

where $\alpha = \sigma^*/\sigma_m$; $\beta = (\alpha - 1)/(\alpha + 2)$ and $F(\alpha)$ is a function derived from the exact solution. MFA and SCA yield closed form solutions (MFA gives the Maxwell equation) which expanded to second order in the volume fraction give:

$$\frac{\sigma^*}{\sigma_m} = 1 + 3\beta v + 3\beta^2 v^2 + O(v^3) \quad \text{MFA} \quad (2)$$

$$\frac{\sigma^*}{\sigma_m} = 1 + 3\beta v + 3\beta^2 [1 + \delta\beta] v^2 + O(v^3) \quad \text{SCA} \quad (3)$$

TABLE I. Composite of simple spherical particles. Coefficient of v^2 in the expansion of σ^*/σ_m : from MFA, SCA, and Jeffrey, Ref. 5.

α	β	coefficient of v^2		
		MFA	SCA	Ref. 5
0	-0.5	0.75	0.66	0.59
0.1	-0.43	0.55	0.50	0.45
1	0	0	0	0
5	0.57	0.97	1.10	1.23
50	0.94	2.65	3.22	3.90
∞	1	3	3.69	3.76

In Eq. (3), $\delta = (R_1/R)^3$ where R is the particle radius and R_1 is the as yet unspecified radius of a concentric shell devoid of particle centers. Numerical computations in Ref. 5 have shown that the coefficient of v^2 in Eq. (3) is very close to the coefficient in Eq. (1) when δ varies between 0.21 and 0.25, depending on the value of α . Table I compares the coefficients of MFA and SCA with the exact coefficient at different values of α . For a fair comparison δ is fixed at the value 0.23 throughout which corresponds to $R_1/R = 1.63$. The table indicates considerably better accuracy for the SCA.

III. THE SCA AND THE MFA FOR CORE-SHELL PARTICLES AT HIGHER VOLUME FRACTIONS

Figure 1(a) shows a core-shell particle having core radius R and shell radius R_1 immersed in some uniform field E' directed along the the x-axis. The core, shell, and matrix conductivities are $\sigma_c, \sigma_s, \sigma_m$ respectively. Figure 1(b) shows a simple particle with conductivity $\hat{\sigma}$. Palla and Jiordano, Ref. 15 show that the particles in Figures a and b are equivalent in the application of the MFA when the conductivity in $\hat{\sigma}$ is defined by

$$\hat{\sigma} = \sigma_s \left[2(1 - c)\sigma_s + (1 + 2c)\sigma_c \right] \left[(2 + c)\sigma_s + (1 - c)\sigma_c \right]^{-1} \quad (4)$$

where $c = (R/R_1)^3$. This “internal homogenization” step simplifies notation and will be used here as well. Eq. (4) agrees with Sihvola, Ref. 1, result for the permittivity of a “layered sphere” and the analogous result for the permittivity of a coated sphere given in Chettiar and Engeta, Ref. 14. The internal homogenization step is valid for MFA and SCA but not for derivations involving solution of the two sphere problem.

The set-up for the MFA and SCA is shown in Figure 2a, b. Consider a large volume of composite containing uniform spherical particles of conductivity $\hat{\sigma}$ imbedded in a matrix of conductivity σ_m under an external field E_{ex} directed along the x axis. The following two equations are exact being simply the definition of average quantities:

$$E_{ex} = \langle \mathbf{E} \rangle = v \langle \mathbf{E} \rangle_P + (1 - v) \langle \mathbf{E} \rangle_M \quad (5)$$

$$J = \sigma^* E_{ex} = \hat{\sigma} v \langle \mathbf{E} \rangle_P + \sigma_m (1 - v) \langle \mathbf{E} \rangle_M \quad (6)$$

where the subscripts P, M denote averages within the particles and the matrix respectively, E_{ex} is the externally imposed field (in the x-direction), J is the macroscopic current (in the x direction), v is the particle volume, and σ^* is by definition the effective conductivity.

A. MFA equations

In MFA $\langle \mathbf{E} \rangle_M$ in Eqs. (5) and (6) is replaced by the as yet unspecified mean field E_{mf} giving the approximate equations

$$E_{ex} = \langle \mathbf{E} \rangle = v \langle \mathbf{E} \rangle_P + (1 - v) E_{mf} \quad (7)$$

$$J = \sigma^* E_{ex} = \hat{\sigma} v \langle \mathbf{E} \rangle_P + \sigma_m (1 - v) E_{mf} \quad (8)$$

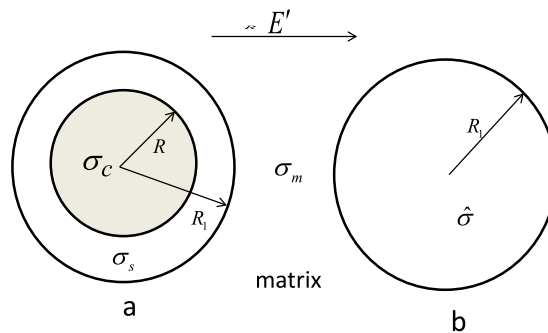


FIG. 1. Core-shell particle (a) and equivalent simple particle (b).

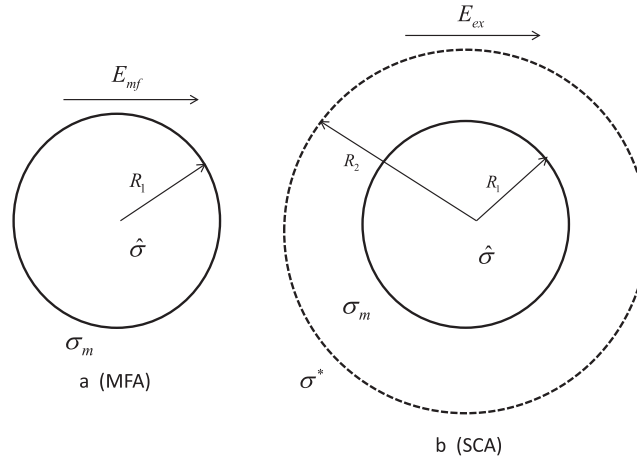


FIG. 2. Specification of conductivities and fields in MFA (a) and SCA (b).

Eliminating E_{mf} gives

$$\sigma^* E_{ex} = (\hat{\sigma} - \sigma_m) v \langle \mathbf{E} \rangle_p + \sigma_m (1 - v) E_{ex} \quad (9)$$

The average field inside the particle is derived in Ref. 15 from the well-known potential equations as

$$\langle \mathbf{E} \rangle_p = - \langle \partial u / \partial x \rangle_p = 3 \sigma_m E_{mf} / (2 \sigma_m + \hat{\sigma}) \quad (10)$$

Introducing (10) in (7) yields $E_{mf} = E_{ex} / (1 - \rho v)$ where $\rho = (\hat{\sigma} - \sigma_m) / (\hat{\sigma} + 2 \sigma_m)$. Introducing this value of E_{mf} into Eqs. (9) and (10) yields the effective conductivity as:

$$\sigma^* = \sigma_m \frac{1 + 2 \rho v}{1 - \rho v} \quad (11)$$

which is simply Maxwell's equation with $\hat{\sigma}$ the particle conductivity.

B. SCA equations

The key premises of the SCA are (i) introduction of a concentric region $R_1 \leq r \leq R_2$ devoid of particle centers and having conductivity σ_m (ii) assignment of the effective conductivity σ^* throughout $r \geq R_2$. The radius R_2 is empirical but can be reasonably chosen as $R_2/R_1 = 1.63$ by the rationale given in section II. Implementation of SCA starts from the exact Eqs. (5) and (6) by eliminating $\langle \mathbf{E} \rangle_M$ to obtain Eq. (7) once more, but this time with $\langle \mathbf{E} \rangle_p$ obtained from a different set of potential equations based on Figure 2b and given in the Appendix. Introducing $\langle \mathbf{E} \rangle_p$ from Eq. (A8) into Eq. (7) gives the working SCA equation

$$\sigma^* / \sigma_m = 1 + (\sigma^* / \sigma_m - 1) A v \quad (12)$$

with A given by Eq. (A8). Eq. (12) is quadratic in σ^* / σ_m and can be solved directly or by simple iteration.

IV. NUMERICAL COMPARISON OF MFA AND SCA

Replacing the core-shell particle with a simple particle of conductivity $\hat{\sigma}$ reduces the MFA problem to one of finding σ^* / σ_m as a function of the variables $\hat{\sigma} / \sigma_m, v$. CSA involves the additional variable R_1/R_2 but having restricted this ratio by using the optimal $(R_1/R_2)^3 = 0.23$ reduces the independent variables to $\hat{\sigma} / \sigma_m, v$. Table I lists $\sigma^* / \sigma_m - 1$ obtained by MFA and SCA for different values of $\hat{\sigma} / \sigma_m$ and v . The results from the two approximations are very close at volume fractions below 0.2 but differ with increasing v and $\hat{\sigma} / \sigma_m$. The closeness of the results at low v is obviously due to the equality of the first order term between MFA and SCA according to Eqs. (1), (2). The first order coefficients are also equal *at all values of c* in the case of core-shell particles. It would be interesting to remove the common first order term and compare the quantity $\Delta = \sigma^* / \sigma_m - 1 - 3 \beta v$

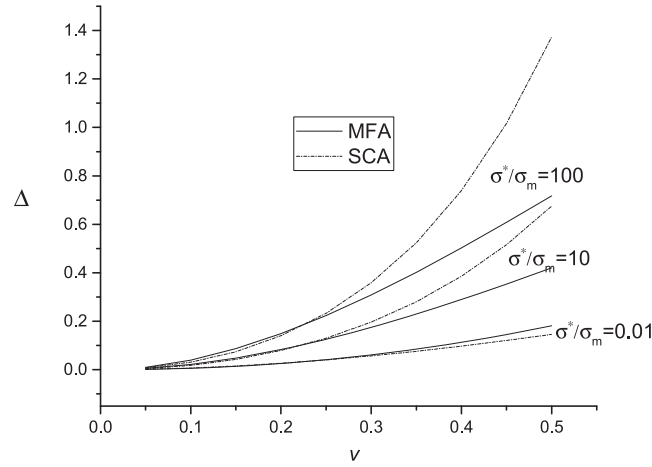


FIG. 3. Residual $\Delta = \sigma^*/\sigma_m - 1 - 3\beta\nu$ from MFA and SCA versus V at different values of σ^*/σ_m .

in the two approximations as a function of ν at different values of $\hat{\sigma}/\sigma_m$. Here 3β is the first order coefficient with $\beta = (\hat{\sigma} - \sigma_m)/(2\sigma_m + \hat{\sigma})$. This comparison is presented in Figure 3 and shows large differences at all volume fractions when σ^*/σ_m is above 10.

V. DISCUSSION AND CONCLUSION

Both the MFA and the SCA attempt to take into account particle-particle interactions beyond the dilute limit. The attempt in both cases is to account for the radial variation of the average field around each particle. In the dilute limit this variation is confined to a limited volume around the particle. At higher volume fractions the field variation extends further beyond the particle surface. To compensate for this radial variation MFA introduces a mean field that extends from the particle surface to infinity but is lower than the external field. The SCA instead introduces a particle-devoid concentric layer $R_1 \leq r \leq R_2$ beyond which the external field applies. As mentioned earlier for simple particles an optimal value of the ratio R_2/R_1 yielded SCA results very close to exact results up to second order in the volume fraction. By contrast, MFA yields a second order coefficient that differs appreciably from the exact results. On that basis the SCA seems to offer higher accuracy for estimating the effective conductivity.

The previously determined optimal value for R_2/R_1 was also used for core-shell particles where exact results to second order are not available. Numerical comparisons show that MFA and SCA differ appreciably above volume fraction 0.3, the difference increasing with the value of the conductivity ratio $\hat{\sigma}/\sigma_m$.

APPENDIX: DERIVATION OF $\langle E \rangle_p$ FOR SCA

The potentials in the three regions of Figure 2b are:

$$u_P = Cr \cos \theta; \quad u_I = (Sr + T/r^2) \cos \theta; \quad u_M = (-E_{ex}r + Q/r^2) \quad (A1)$$

and are associated with the compatibility conditions:

$$r = R_1: \quad u_P = u_I; \quad \hat{\sigma} u_P = \sigma_m u_I \quad (A2)$$

$$r = R_2: \quad u_I = u_M; \quad \sigma_m u_I = \sigma^* u_M \quad (A3)$$

Solution of these equations yields the coefficients:

$$C = C_1 T'; \quad S = S_1 T' \quad (A4)$$

$$C_1 = \frac{3\sigma_m}{(\sigma_m - \hat{\sigma})}; \quad S_1 = \frac{2\sigma_m + \hat{\sigma}}{(\sigma_m - \hat{\sigma})} \quad (A5)$$

$$T' = -3\sigma^* [S_1(\sigma_m + 2\sigma^*) + 2c(\sigma^* - \sigma_m)]^{-1} E_{ex} \quad (\text{A6})$$

where $c = (R_1/R_2)^3$. Using these constants the average field in the particle is

$$\langle E \rangle_P = -\langle \partial u / \partial x \rangle_P = C = A E_{ex} \quad (\text{A7})$$

where

$$A = 9(\sigma^* / \sigma_m) [(1 + 2\sigma^* / \sigma_m)(2\sigma_m + \hat{\sigma}) + 2c(\sigma^* / \sigma_m - 1)(1 - \hat{\sigma} / \sigma_m)] E_{ex} \quad (\text{A8})$$

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